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# **GASIFICATION OF CHARS PRODUCED UNDER SIMULATED in situ PROCESSING CONDITIONS**

**Quarterly Report for the Period  
January—March 1976**

**by**

**J. Fischer, J. E. Young, R. Lo,  
J. E. Johnson, and A. A. Jonke**

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9700 South Cass Avenue  
Argonne, Illinois 60439

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# GASIFICATION OF CHARS PRODUCED UNDER SIMULATED *IN SITU* PROCESSING CONDITIONS .

J. Fischer, J. E. Young, R. Lo,  
J. E. Johnson, and A. A. Jonke

## ABSTRACT

This effort, which is part of the Argonne National Laboratory energy program for ERDA, is being directed toward support studies for the national endeavor on *in situ* coal gasification. This task involves the investigation of reaction-controlling variables and product distributions for the gasification of both coals and chars utilizing steam. Preliminary runs are currently being carried out on the high pressure char gasification system in order to determine optimum operating conditions; results are described and discussed. The procedures for analysis of product gas have been developed and are also described.

## SUMMARY

This task has the objectives of providing engineering data and analyses for char gasification by steam under simulated *in situ* processing conditions. The coal samples will be representative of coal at sites being considered for *in situ* gasification field tests. Chars for gasification will be made by pyrolyzing coal from several sources at the low heating rates characteristic of *in situ* gasification processes. The results will be interpreted in terms of field design and resource recovery; thus this work will support the major field projects in the ERDA *in situ* coal program.

Analytical procedures have been developed to analyze the product gases for  $H_2$ ,  $N_2$ ,  $CO$ ,  $CH_4$ , and  $CO_2$ . An automated gas chromatographic analyzer is used, allowing a complete analysis to be carried out in approximately 7 min.

Initial experiments have been carried out to investigate the reaction of steam with char prepared from Wyodak-Anderson subbituminous coal. The purpose of these early runs is to determine the operating conditions necessary to yield differential conversion rates (*i.e.*, conversion of less than 1% of the input reactant gases). However, product gas concentrations should be sufficiently high to establish a high confidence in the chromatographic analytical data.



## INTRODUCTION

The objective of this project is to determine how the reaction-controlling variables affect the reaction kinetics for the gasification of coals and chars resulting from the pyrolysis of coal in underground gasification. This work is relevant to all of the underground gasification projects being funded by ERDA. The data obtained from this work will be used in modeling *in situ* gasification systems, in order to understand and interpret field experimental data, and will be used in the design of future field experiments.

In the gasification of coal and char with steam utilizing a laboratory-scale gasifier (described earlier),<sup>1</sup> a number of variables are being investigated that are representative of actual *in situ* gasification conditions. These variables include total pressure during gasification reaction temperature during gasification, coal devolatilization conditions, and partial pressure of steam. Quantitative analyses of gaseous product constituents such as hydrogen, methane, higher hydrocarbons, carbon monoxide, and carbon dioxide are performed to enable calculation of the Btu value of the product gas. In the future, a special series of gasification runs will be carried out to investigate the effects of utilizing brackish water for the steam supply.

During this reporting period, initial gasification experiments have been carried out in order to optimize operating variables such as char sample size, feed rate of steam, and feed rate of inert carrier gas. The results of two of these runs are reported and the system for analysis of product gas is described.

## ANALYTICAL SYSTEM FOR PRODUCT GASES

In our experiments, the product gas from gasification of char contains steam, nitrogen, CO, CO<sub>2</sub>, H<sub>2</sub>, and methane. The chars used in these experiments contain only a small percentage of volatile matter, and it is not expected that hydrocarbons heavier than methane will be produced. Nitrogen is introduced as an inert carrier gas flowing through the reactor. Unreacted steam in the product stream is condensed and separated from the reactor. Any remaining water vapor is removed with Drierite. Hydrogen sulfide is produced from any sulfur in the char during steam gasification. An analytical procedure has been developed which will give quantitative data for H<sub>2</sub>, N<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>S.

The analysis of the product gas is carried out utilizing a Hewlett Packard Model 5830A gas chromatograph equipped with thermal conductivity detectors. This unit is programmed for automatic operation of the gas sampling valves, switching of the detector signals, and integration and calculation of the concentrations of the chemical constituents. The data processing section of this chromatograph is also compatible with data logging equipment to be installed in the future.

The flow system of the chromatograph is shown in Fig. 1. Two chromatographic columns are used, each supplied by a six-port sampling valve with 0.5 cm<sup>3</sup> sampling loops. At present, helium is used as the carrier gas. This presents problems regarding the analysis for hydrogen (the details of which are discussed later in this section). Column A is a 4 ft by 1/8-in.-OD by 0.085-in.-ID stainless steel column containing 80/100 mesh type



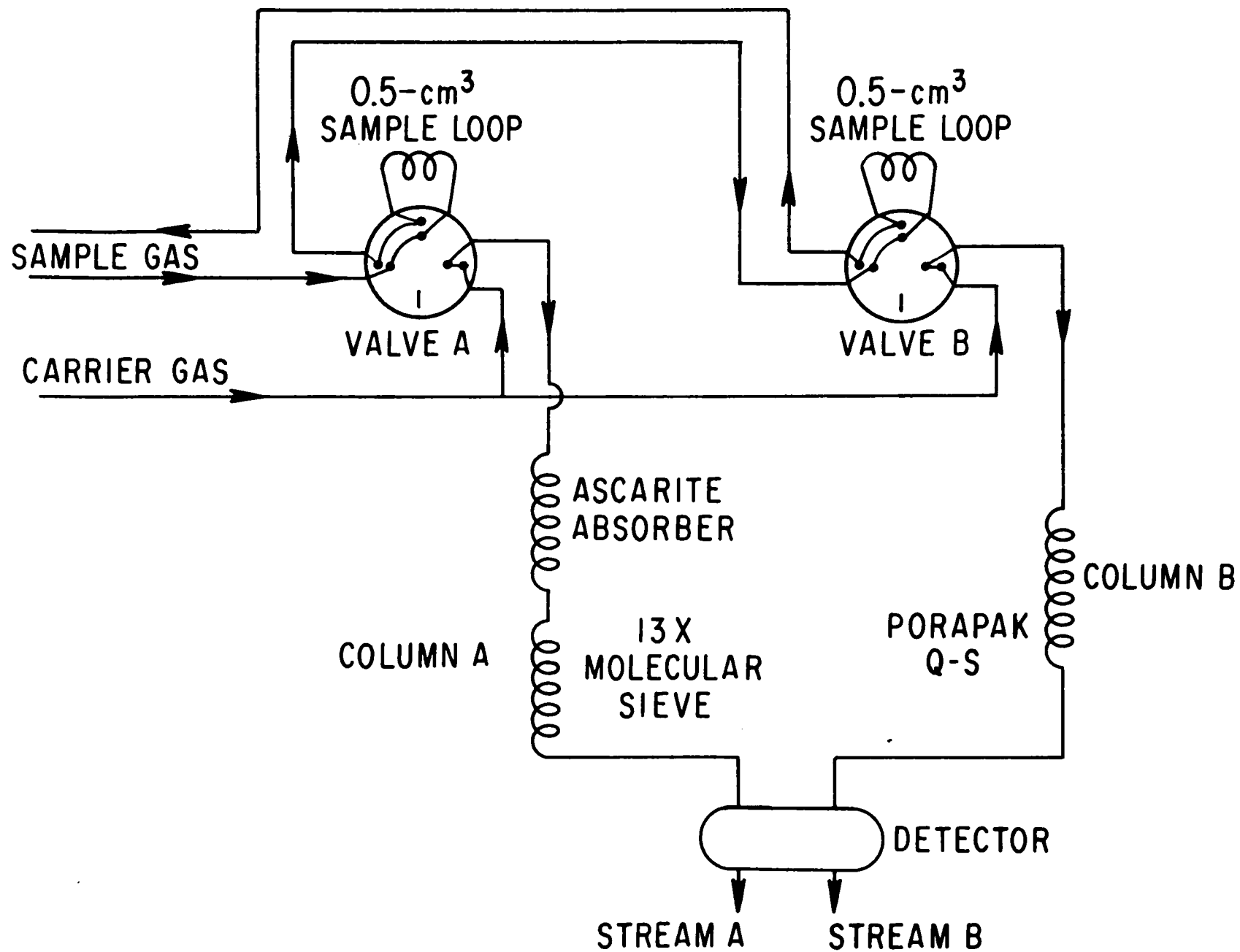


Fig. 1. Gas Chromatograph Flow Diagram.

13X Molecular Sieve. This column separates  $H_2$ ,  $N_2$ ,  $CO$ , and  $CH_4$  from the other gaseous constituents. Contamination of this column by  $CO_2$  and  $H_2S$  is prevented by inserting upstream from it an absorber consisting of a 1-ft by 3/16-in.-OD by 1/8-in.-ID stainless steel tube containing Ascarite. The Ascarite consists of sodium hydroxide on an inert support, and permanently absorbs any acid gases ( $CO_2$  or  $H_2S$ ).

Column B is a 6-ft by 1/8-in.-OD by 0.085-in.-ID stainless steel column containing 80/100 mesh Porapak Q-S. This column separates  $CH_4$ ,  $CO_2$ , and  $H_2S$  from the other gaseous constituents. Both columns are operated at  $35^\circ C$ , with a carrier gas flow of  $20 \text{ cm}^3/\text{min}$ . The thermal conductivity detector is operated at  $100^\circ C$ .

The operating sequence is as follows: With the integrator monitoring detector signal A, sampling valve A is energized. The sample passes through the Ascarite absorber, where  $CO_2$  and  $H_2S$  are removed. The  $H_2$ ,  $N_2$ ,  $CO$ , and  $CH_4$  are then separated in the 13X Molecular Sieve column. The gaseous constituents are eluted in the order,  $H_2$ ,  $N_2$ ,  $CH_4$ , and  $CO$ . The  $CO$  is no longer detected, sample valve B is energized and the integrator is switched to detector signal B. All gaseous constituents are carried into the Porapak Q-S column. However,  $H_2$ ,  $N_2$ , and  $CO_2$  are not separated and are detected as a single peak. First the  $CH_4$ , then the  $CO_2$ , and then the  $H_2S$  are eluted.

A typical chromatogram is shown in Fig. 2. The gas analyzed in Fig. 2 is a sample of a calibration gas mixture containing 2.03%  $H_2$ , 2.09%  $CO$ , 0.987%  $CH_4$ , 1.96%  $CO_2$ , and the balance nitrogen. At time 0.1 min, sample valve A is energized. The hydrogen peak elutes at 0.71 min. The peak at 0.93 min is due to oxygen impurity of approximately 100 ppm. The peak due to nitrogen occurs at 1.15 min. The peak due to  $CH_4$  is found on the tail of the nitrogen peak at 1.85 min.  $CO$  is eluted at 2.65 min. At 3.50 min, the detector signal is switched and sample valve B is energized. The square peak on the chromatogram at this time is a perturbation caused by the switching of the detector signal, and is not included in the total area calculation. The large peak at 3.99 min is due to a combustion of  $H_2$ ,  $N_2$ , and  $CO$ . At 4.21 min, methane is eluted and at 4.71 min the  $CO_2$  is detected. If  $H_2S$  is present in the sample, its peak is obtained at approximately the 8-min mark.

As can be seen in Fig. 2, two methane peaks are obtained. Either peak is of adequate quality for use in the area integration, but that obtained with the Porapak Q-S column is sharper and the beginning and end points of the integration are more clearly defined. Therefore the latter peak is used for the methane calculation.

The use of helium as the carrier gas results in reduced sensitivity of the thermal conductivity detectors for hydrogen. The hydrogen peak in Fig. 2, corresponding to 2% hydrogen, has an area more than a factor of 40 less than those due to  $CO$  or  $CO_2$ , which also correspond to approximately 2% concentrations. This is because the thermal conductivity of hydrogen is very close to that of helium.

In addition to the lack of sensitivity, the thermal conductivity of hydrogen-helium mixtures is not linear with respect to concentration. The thermal conductivity of hydrogen is  $471 \times 10^{-6} \text{ cal}/(\text{sec})(\text{cm}^2)(^\circ C/\text{cm})$  at  $50^\circ C$ :

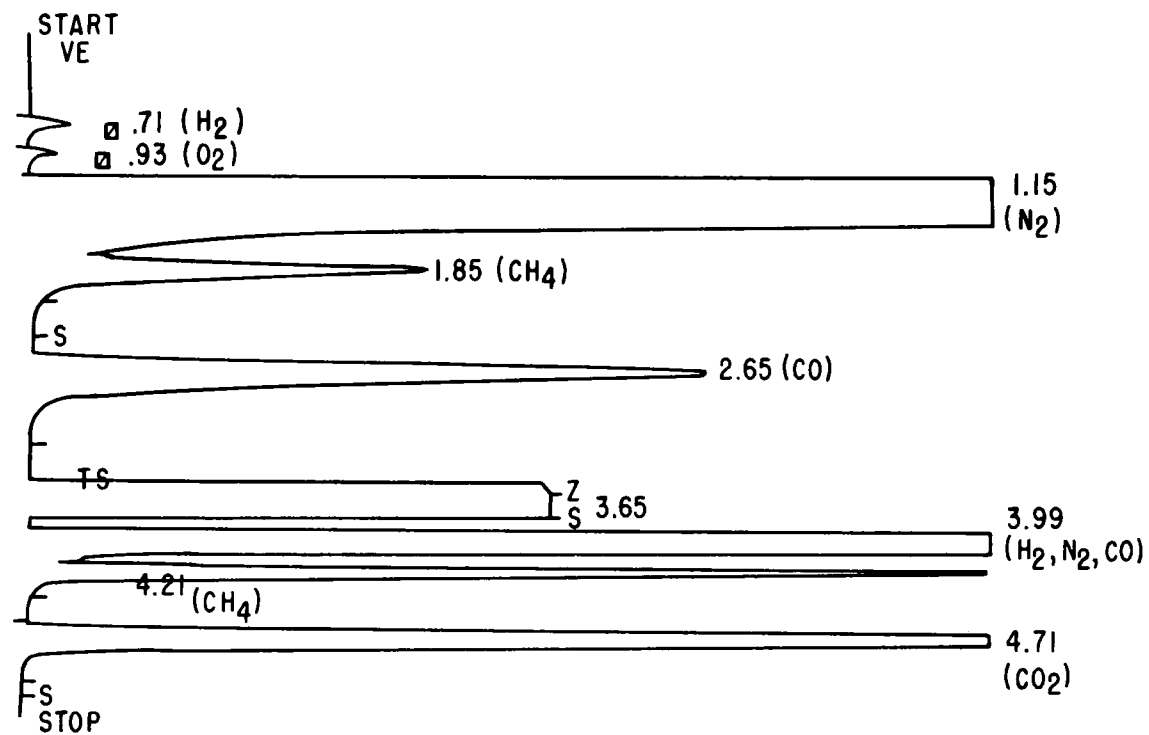


Fig. 2. Recorder Trace from Gas Chromatograph

that of helium, is  $376 \times 10^{-6}$  cal/(sec)(cm<sup>2</sup>)(°C/cm) at 50°C. However, when hydrogen is blended with helium, the thermal conductivity of the mixture decreases rather than increases. The conductivity of the mixture reaches a minimum at approximately 8% hydrogen in helium, and then increases as the concentration of hydrogen increases further.

If the concentration of hydrogen in the helium is kept low, a reasonably linear calibration curve can be obtained. The calibration graph used in the present determinations is shown in Fig. 3. Also included in this figure are the calibrations for CO<sub>2</sub>, CH<sub>4</sub>, and CO in the product gas. The response of the detector for all of the gas constituents is reasonably linear for the concentration ranges of 0-2% for H<sub>2</sub>, CO, and CO<sub>2</sub> and of 0-1% for CH<sub>4</sub>. For the present calculations, the detector response is assumed to be linear. More precise calibration curves will be determined after final concentration ranges are established for operation of the gasification reactor system.

If the hydrogen concentration rises above the 2% level, there will be nonlinearity in the calibration curve. In fact, when the concentration of hydrogen reaches 8% in the carrier gas, an anomaly will appear in the chromatogram in the form of a splitting of the hydrogen peak. This can be avoided by using as the carrier gas a blend of helium and hydrogen having a hydrogen concentration greater than 8%. Then, hydrogen added to the carrier would cause the thermal conductivity to increase linearly as a function of hydrogen concentration. However, if the hydrogen-helium blend is used as carrier gas, the sensitivity of the detector is still very poor.

The use of nitrogen or argon as carrier gas would give excellent sensitivity for hydrogen, but the thermal conductivity of nitrogen is nearly identical to that of CO, and the thermal conductivity of argon is nearly equal to that of CO<sub>2</sub>. Hence, one or the other of peaks would be lost if nitrogen or argon were used. In the near future, a number of tests will be made in which neon will be used as the carrier gas. This will result in the sensitivity for hydrogen being greatly improved but the sensitivity for the other constituents being somewhat reduced. Since the chromatograph has more than adequate sensitivity for all constituents other than hydrogen, neon should be a good alternative to the other carrier gases.

Analysis for H<sub>2</sub>S using the present chromatograph column configuration results in a very broad peak and with relatively longer retention times than for the other constituents of the product gas. For this reason, a separate analyzer will be obtained for H<sub>2</sub>S analysis, and the gas chromatograph will be used for constituents other than H<sub>2</sub>S.

#### CHAR GASIFICATION EXPERIMENTS

At present, experiments are being carried out in the char gasifier system previously described.<sup>1</sup> These experiments involve the reaction of steam with chars prepared from Wyodak-Anderson subbituminous coal. Their purpose is to optimize a number of operating conditions such as char sample bed dimensions, steam injection rate, and nitrogen sweep gas flow rate.

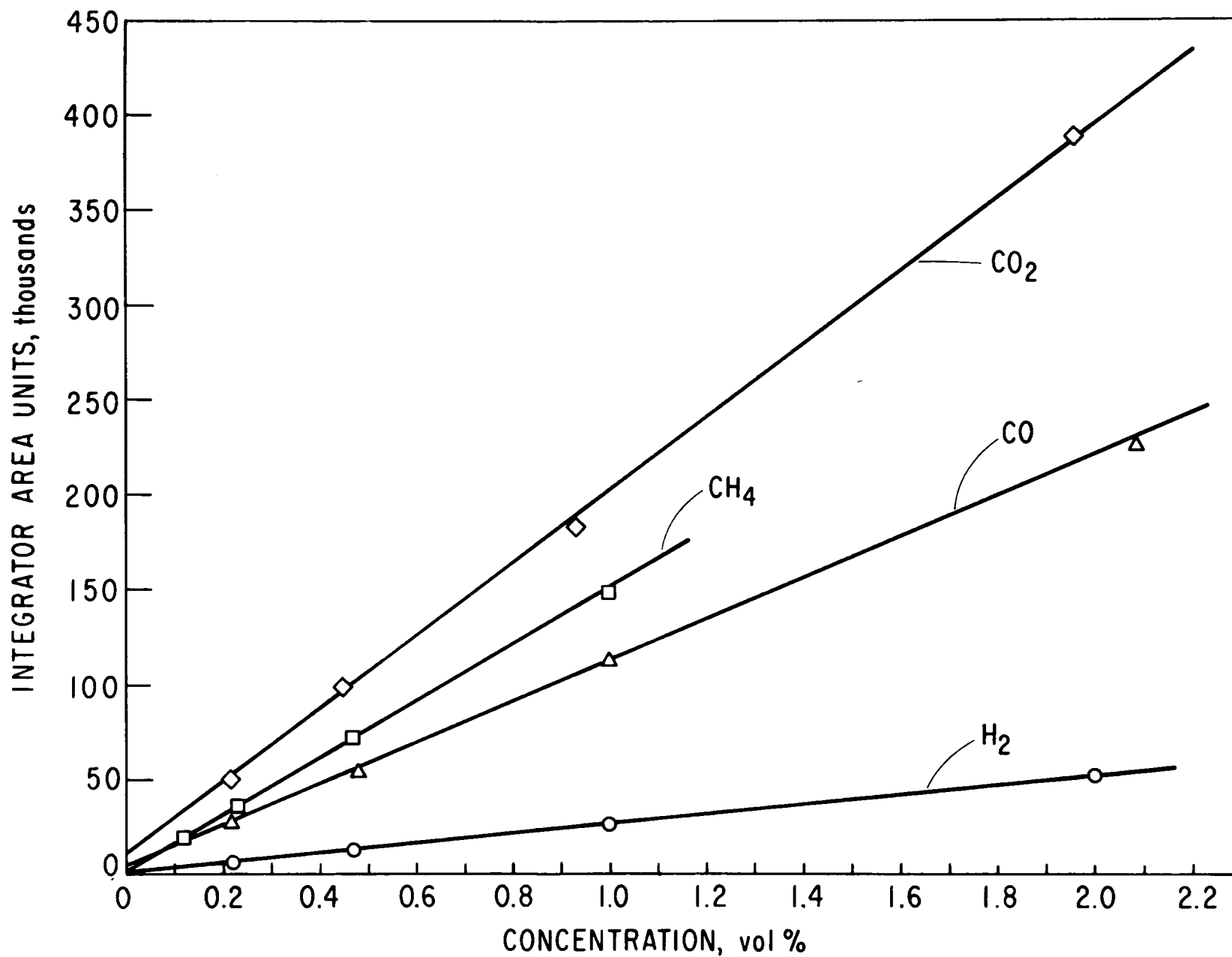


Fig. 3. Calibration Data Helium Carrier Gas.

These experiments are being carried out in a down-flow differential packed-bed reactor. In order to ensure differential conditions, the space velocity must be kept high.

The length of the vertical gasifier reactor is 91 cm. The depth of the char bed is expected to be between 1 and 10 cm. In an experiment, the reactor is loaded with 120-mesh electrically fused crystalline alumina to a depth of approximately 45 cm. The char is placed on top of the initial loading of alumina and then the remainder of the reactor space is filled with 8-mesh alumina. The upper portion of the reactor (filled with the 8-mesh alumina) serves as a preheater section to increase the steam and nitrogen carrier gas temperature to reaction temperature. During reactor heatup, the steam generator output bypasses the reactor and flows directly into the downstream condenser and separator.

Figure 4 shows the product gas analysis results for a run using a 10-cm<sup>3</sup> (5-cm-deep) bed of char. The char for this experiments was obtained from Wyodak-Anderson subbituminous coal. The coal was crushed to -60 mesh and pyrolyzed in a flowing nitrogen atmosphere (1-atm pressure) to produce the char. The heating rate for pyrolysis was 3°C/min, and the char was held at the final temperature of 800°C for 2 hr before cooling. The char was then transferred to the gasification reactor in a nitrogen-filled glove bag and then sealed.

Preparation of the char outside the gasification reactor is being done only in these initial studies. The temperature cycling (between pyrolysis and gasification), as well as possible exposure to traces of oxygen during transfer to the reactor, undoubtedly affect the structure and reactivity of the char. When optimum gasification operating conditions are defined, coal pyrolysis will be carried out in the gasification reactor, eliminating any temperature cycling or aging effects.

In the run shown in Fig. 4, the char was heated in a nitrogen flow of 1.6 liters/min STP. Within 100 min, the reactor was heated and stabilized at the desired reaction temperature. During reactor heatup, the steam generator output bypasses the reactor and flows directly into the downstream condenser and separator. During the final stages of reactor heatup, very small amounts of H<sub>2</sub>, CO, and CO<sub>2</sub> are obtained from the char reactor. This is probably due either to reaction with moisture adsorbed on the char and the reactor during reactor charging, or to steam leaking into the reactor through the bypass valves. Leakage of these bypass valves will be checked in the near future.

At 100 min, steam was fed to the reactor at a rate of 3.93 mol/hr. Total system pressure was 16 atm absolute; the partial pressure of steam was 8.0 atm. The initial reaction was very rapid. In fact, the concentrations of product gases at the reactor outlet were well above the calibrated range of the gas chromatograph. The hydrogen concentration rose to a level such that the gas chromatograph signal peak was split due to previously mentioned anomalies in the hydrogen-helium thermal conductivity relationship; hence, the hydrogen analysis for the early stages of this run was not recorded.

From the production rate of carbon oxides, it was calculated that the rate of conversion of the steam exceeded 25% during the early stages of

gasification. In addition, a temperature differential of 30°C was observed across the bed. Obviously, under these reactor conditions, conversion rates were too high for meaningful kinetic analysis of the data. When the reactor was dismantled after the run, it was observed that the char bed had been entirely consumed.

An additional problem was observed during this run. The starting material for preparation of the char sample was -60 mesh. After pyrolysis, this sample contained a rather large fraction of material 200 mesh or finer. As a result, a pressure drop of nearly 50 psi developed across the bed. Use of particles of this size would make very difficult the separation of char from the 120-mesh alumina inert packing material. This separation would be necessary to obtain a carbon balance.

Run 5 was made under conditions modified to alleviate some of the problems encountered in Run 4. In order to increase the space velocity, the char bed size was reduced from 10 cm<sup>3</sup> to 2 cm<sup>3</sup>. The particle size for Run 5 was -20 +60 mesh. The source of the char for this run (previously obtained from Oak Ridge National Laboratory) was Wyodak-Anderson subbituminous coal. The char was the product from a large-coal-block pyrolysis experiment carried out at Oak Ridge (Run BP-8) in which the nominal heating rate was 3°C/min, and the final pyrolysis temperature was 800°C. Because this char had been exposed to air during shipment to ANL, no precautions were taken to prevent air exposure during transfer into our gasification reactor.

For Run 5, the nitrogen flow rate was 2.4 liters/min STP; the reaction temperature was 700°C, and the water pumping rate for steam generation was 92.8 cm<sup>3</sup>/hr. Total system pressure was 16 atm absolute; the partial pressure of steam was 7.3 atm.

The product gas analysis data are shown in Fig. 5. It is apparent from these data that the reaction occurs in at least two steps. A portion of the char is extremely active, but this part is depleted quite rapidly. At approximately the 60-min mark, the rate changes radically and remains nearly constant. As calculated from the total carbon-containing gases produced, 32% of the carbon was gasified in the initial 60-min period. When the run was terminated at 180 min, 50% of the carbon had been gasified. An additional change in the reaction rate was observed at 140 min. No anomalies in reaction conditions (gas flows, etc.) were observed. This rather small change in apparent rate must be reproduced before it can confidently be ascribed to an actual change in reactivity.

It is apparent from both Runs 4 and 5 that the water gas shift reaction is occurring to a great extent. Under the reaction conditions used in these experiments, the very high partial pressure of steam should shift the equilibrium well towards the CO<sub>2</sub> + H<sub>2</sub> product. The mineral matter in this char apparently has sufficient catalytic activity to ensure near-equilibrium concentrations of product gases for this reaction despite the relatively short contact time with the char bed (0.12 sec in the case of Run 5). A detailed analysis of the kinetics of this reaction is planned in the near future.

An additional factor affecting the water gas shift equilibrium is the reactor material itself (type 316 stainless steel). The iron content of the reactor may be catalyzing the shift reaction. The residence time of the



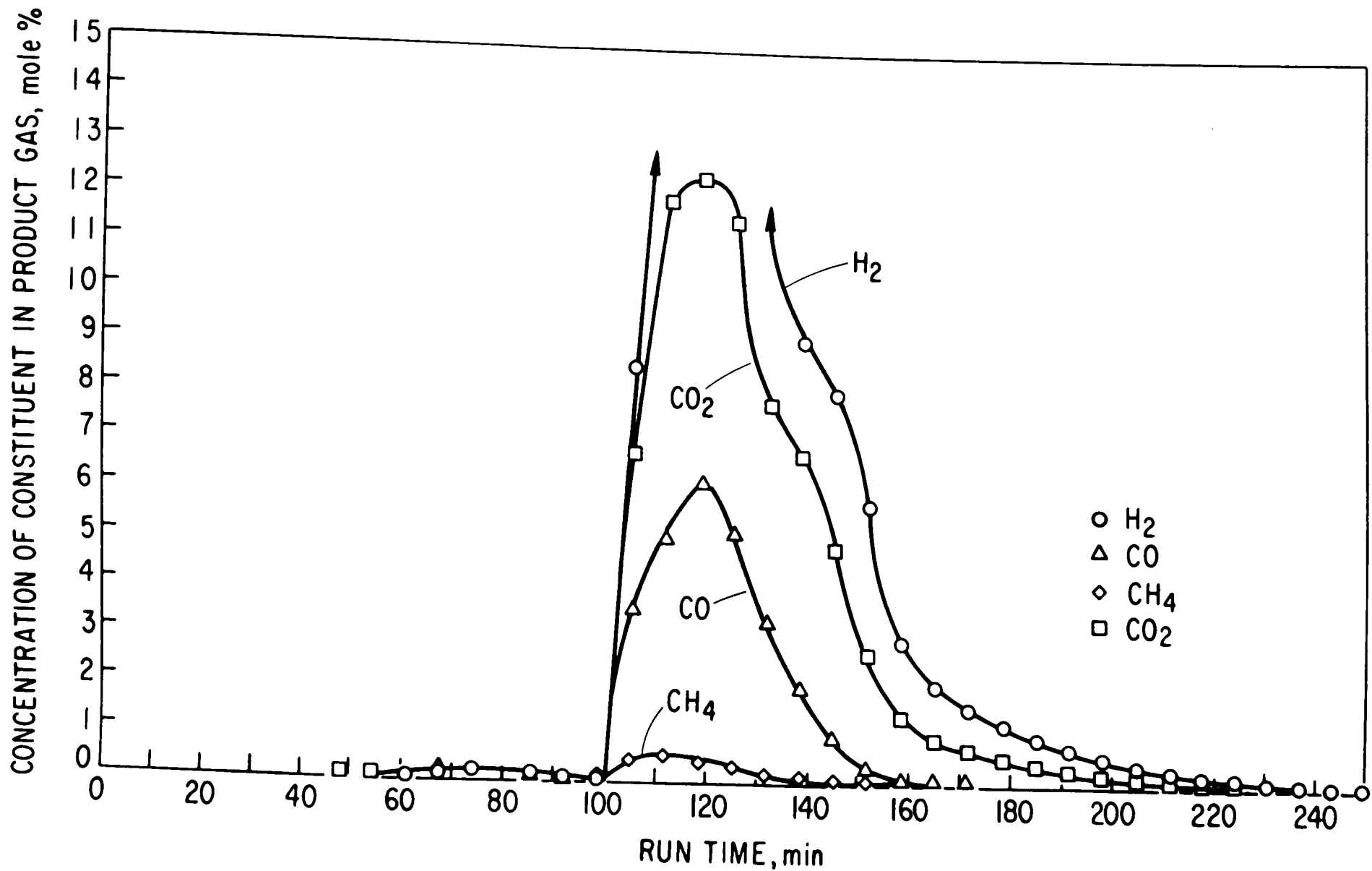


Fig. 4. Steam-Char Gasification for Run 4.

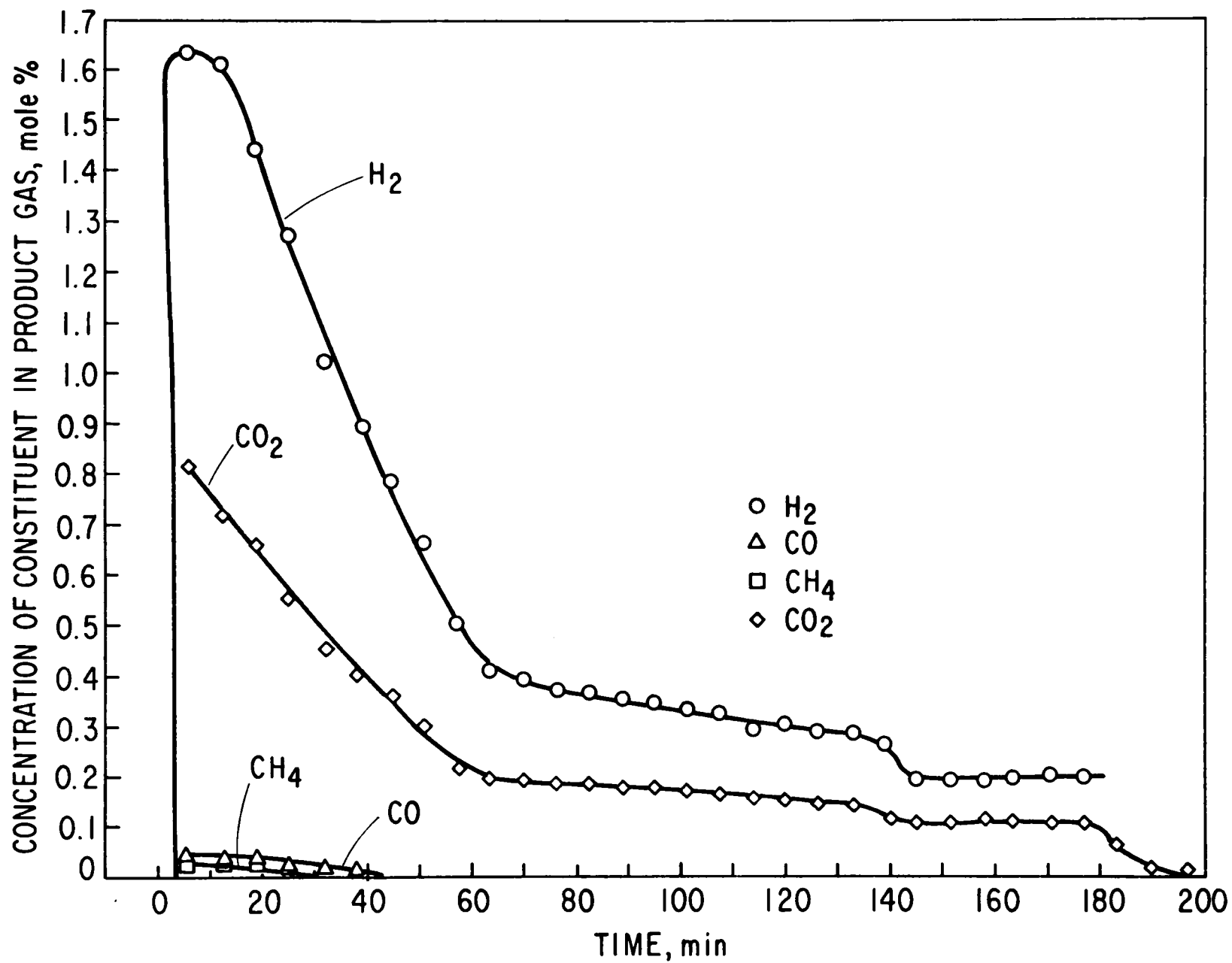


Fig. 5. Steam-Char Gasification for Run 5.

product gases in the reactor downstream from the char bed is approximately 8 sec - a relatively long time. The contribution of the reactor wall material to catalysis of this reaction will be determined by means of blank runs (in the absence of a char bed) during the next quarter.

#### REFERENCE

1. J. Fischer, R. Lo, J. Young, and A. Jonke, Gasification of Chars Produced Under Simulated *in situ* Processing Conditions, Quarterly Report for the Period October-December, 1975, ANL-76-3.



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